
INCORPORATION OF PORE NETWORK CONNECTIVITY ON THE PREDICTION OF BINARY LIQUID PHASE ADSORPTION OF FLAVOUR ESTERS IN ACTIVATED CARBON

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Submitted 14 Mei 2004, reviewed 20 Mei 2004, and accepted 19 Maret 2005

Abstract

The structural heterogeneity of activated carbon is a result of the existence of micropores, mesopores, and macropores of different sizes and shapes, randomly connected in a pore network. In a pore network, some of the pores that are large enough to accommodate the probe molecules may be accessible through smaller pores that only permit the passage of probe molecules having a smaller size. In the adsorption process, especially involving large and complex probe molecules, the pore network connectivity is very important, and governs the transport and reaction properties of the pores. A method for incorporation of the pore network connectivity along with IAST (Ideal Adsorbed Solution Theory Method) on the prediction of binary component adsorption isotherm is proposed in this article. IAST is used in conjunction with the modified DR (Dubinin-Radushkevich) single component isotherm, and is found that the incorporation of the connectivity can improve the accuracy of model in predicts the multicomponent adsorption performance.

Keywords: Adsorption, IAST, Pore Network Connectivity

Abstrak

Pore network connectivity memegang peranan yang penting dalam proses adsorpsi yang melibatkan senyawa senyawa kompleks. Pada makalah ini diusulkan suatu metode yang menggabungkan Pore network connectivity dan persamaan IAST untuk prediksi isotherm adsorpsi senyawa biner. Untuk mendapatkan isotherm adsorpsi dilakukan percobaan dengan menggunakan ethyl propionate dan ethyl butyrate sebagai adsorbate dan sebagai adsorbent digunakan karbon aktif Filtrasorb F-400 dan Norit ROW 0.8. Untuk menggambarkan isotherm adsorpsi dari hasil percobaan digunakan persamaan The Ideal Adsorbed Solution Theory dengan modifikasi persamaan isotherm adsorpsi dari Dubinin-Radushkevich dan Pore network connectivity. Dari hasil yang diperoleh dapat disimpulkan bahwa persamaan yang melibatkan pengaruh pore network connectivity dapat meningkatkan unjuk kerja dari persamaan isotherm multi komponen untuk prediksi data data percobaan adsorpsi biner.

Kata Kunci: Adsorpsi, IAST, Pore Network Connectivity

1. Introduction

Purification and separation of compounds from their mixtures can be carried out by several methods such as distillation, extraction, and adsorption. The adsorption itself now become a standard unit operation in chemical industry since it consumes low energy with separation efficiency comparable to other techniques. The adsorption system usually involves more than one compound and therefore the engineering design of the adsorption process requires information on multicomponent adsorption kinetics and equilibrium properties. As reliable experimental multicomponent adsorption isotherm data at various temperature and concentrations are difficult and time consuming to obtain, it is desirable to have a tool for predicting the multicomponent adsorption based on single component adsorption isotherms. For this purpose, various models and their modifications for describing multicomponent adsorption equilibria have been developed, such as extended Langmuir equation (Choy et al., 2000; Bai, 2000), Freundlich-type multicomponent equation (Fritz & Schlunder, 1974, 1981; McKay & Al-Duri, 1988), ideal adsorbed solution theory and its variants (Myers & Prausnitz, 1965; Radke & Prausnitz, 1972; Porter et al., 1999; Wang et al., 2000), Myers-Prausnitz-Dubinin Theory (Lavancy & Stoeckli, 1999), and other approaches (Buffham et al., 1999). Among these the IAST of Myers and Prausnitz is the most established and widely used method because of its generality and applicability to arbitrary single component isotherms.

For heterogeneous adsorbents such as activated carbon, in many cases, the IAST is inadequate to describe the experimental data because it does not account the structural and chemical heterogeneity which is present in activated carbon, and nonideality of the adsorbed mixture (Ismadji & Bhatia, 2003). The structural heterogeneity of activated carbon is a result of the existence of micropores, mesopores, and macropores of different sizes and shapes, randomly connected in a pore network. In a pore network, some of the pores, that are large enough to accommodate the probe molecules, may be accessible only through smaller pores that only permit the passage of probe molecule having smaller size. Therefore only a part of the available pores is actually accessible to the probe molecules (Ismadji & Bhatia, 2000).

In the adsorption process, especially involving large and complex molecules, the pore network connectivity is very important, and governs the transport and reaction properties of the

pores. In this article, a modification of IAST by incorporating pore network connectivity is proposed. The model is used to describe binary adsorption of large molecules from the liquid phase on activated carbon.

2. Fundamental

The behavior of transport and reaction properties on the porous materials is very strongly affected by the internal structure of porous materials. There are now many different techniques are available for characterizing the structure of porous materials. These techniques are based on direct measurement, such as xenon NMR and size exclusion chromatography, or indirect measurement, such as gas adsorption. To obtain structural information from indirect measurement experimental data, a model of the pore network is required. The most common and simplest concept for characterizing the topology of porous materials based on percolation theory (Ismadji & Bhatia, 2000). In percolation theory, the topology of pore structure is described by the mean coordination number of the pore network Z .

For a given network, the number fraction of the pores that can accommodate a given probe molecule can be written as:

$$\Phi = \frac{\int_0^\infty f(H) / H dH}{\int_0^\infty f(H) / H dH} \quad (1)$$

The fraction of the pores that actually accessible to the probe molecules " is a function of the network topology and coordination number Z , as well as the fraction of available pores.

$$\Phi^a = 0, \Phi \leq (1.494/Z) \quad (2)$$

$$\Phi^a = f(Z, \Phi) \quad (3)$$

$$\Phi^a = \Phi, \Phi \geq (2.7/Z) \quad (4)$$

As mentioned above, one of the simplest way to characterize the network topology and coordination number Z is using adsorption technique. This technique is implemented in this work.

3. Methodology

The problem of pore network accessibility, while straightforward for the single component case, offers additional complexities in multicomponent adsorption of large molecules because of the differences in critical molecular sizes of the different components. To illustrate this, the binary adsorption of two components was considered. Component 1 has a critical molecular size, d_{c1} , which is smaller than critical molecular size of component 2, d_{c2} . The adsorption behavior

of the binary mixture is best described by considering four different groups of pores, as depicted in Figure 1. In the pore size between d_{c1} and d_{c2} ($d_{c1} < H < d_{c2}$), only pure component 1 is present (indicated as region 1 in Figure 1) since the pores in this region are not accessible to component 2.

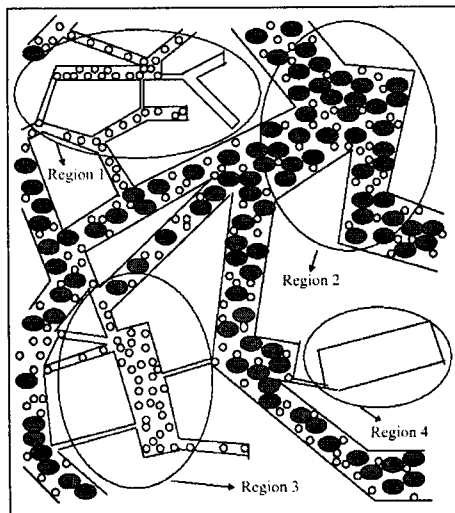


Figure 1. Schematic Diagram of Binary Adsorption Process in Micropore Network

However, although the pores in this region are large enough to accommodate the probe molecules 1, some of these pores are connected through pores which have size smaller than d_{c1} and therefore are not accessible to these probe molecules. The amount of component 1 adsorbed in this region can be expressed as

$$n_{1a} = \frac{\Phi_1^a}{\Phi_1} \int_{d_{c1}}^{d_{c2}} n_1^{pure}(H) f(H) dH \quad (5)$$

where $f(H)$ is the normalized pore volume distribution function, Φ_1 is the fraction of the available pores for component 1 and Φ_1^a is the fraction of the pores that are actually accessible to the probe molecules.

For the pores having size between d_{c2} and d_{c1} , some of them are accessible to both compounds, so that a mixture of components 1 and 2 will be present within these latter pores (region 2). Further, some of the pores larger than d_{c2} are connected by smaller pores that have size smaller than d_{c2} . If the connecting pores have size between d_{c1} and d_{c2} , then the component 1 can access these other larger pores (region 3). If the connecting pores have dimension smaller than d_{c1} , the pores larger than d_{c2} will be inaccessible to both

compounds (region 4). Therefore, the amount adsorbed of component 1 in these regions (region 2 to 4) can be written as

$$n_{1b} = \frac{\Phi_2^a}{\Phi_2} \int_{d_{c2}}^{\infty} n_1^{mix}(H) f(H) dH + \left[\frac{\Phi_1^a}{\Phi_1} - \frac{\Phi_2^a}{\Phi_2} \right] \int_{d_{c2}}^{\infty} n_1^{pure}(H) f(H) dH \quad (6)$$

The total adsorbed amount of component 1 will be equal to $n_{1a} + n_{1b}$, leading to

$$n_{1,tot}^{mix} = \frac{\Phi_1^a}{\Phi_1} \int_{d_{c1}}^{\infty} n_1^{pure}(H) f(H) dH + \frac{\Phi_2^a}{\Phi_2} \int_{d_{c2}}^{\infty} [n_1^{mix}(H) - n_1^{pure}(H)] f(H) dH \quad (7)$$

For component 2 the amount adsorbed is readily given by

$$n_{2,tot}^{mix} = \frac{\Phi_2^a}{\Phi_2} \int_{d_{c2}}^{\infty} n_2^{mix}(H) f(H) dH \quad (8)$$

Equations (7) and (8) are valid for any single and binary component isotherm. A modified Dubinin-Radushkevich model to include bulk nonideality of the liquid phase and the repulsive potential in the micropores is used as the single component isotherm (Ismadji & Bhatia, 2001).

In developing a multicomponent isotherm model, based on the above single component isotherm, the ideal adsorbed solution theory of Myers and Prausnitz (1965) has been utilized. The IAST theory was developed based on the assumption that the adsorbed phase can be treated as an ideal solution of the adsorbed components, and its application usually consider ideal bulk phase as well. For a nonideal bulk fluid, the Gibbs adsorption equation may be written as

$$V d\phi = n_i^{pure} d\mu_i^a = n_i^{pure} RT d \ln(a_i) \quad (9)$$

Where μ_i is the chemical potential of solute i , and ϕ is a three dimensional spreading pressure. Integration of equation (9) leads to

$$\Pi_i = \frac{\phi V}{RT} = \int_0^{a_i''} \frac{n_i^{pure}}{a_i} da_i = \Pi = \text{constant} \quad (10)$$

For the details of equation (10) the reader can refers to Myers and Prausnitz (1965). For the multicomponent adsorbate, if the solute in the bulk solution is in equilibrium with the adsorbed species then follow the equation as below

$$d\mu_i^b = d\mu_i^a \text{ or } RTd \ln(a_i) = RTd \ln(x_i) \quad (11)$$

Where μ_i^b and μ_i^a are the chemical potential of species i in the bulk solution and in adsorbed phase, respectively. Equation (11) can be integrated with the condition of $x_i = 1$ for

$$a_i = a_i^o \text{ to yield } a_i = a_i^o x_i \quad (12)$$

The adsorbed phase compositions must satisfy the requirement

$$\sum_{i=1}^N x_i = 1 \quad (13)$$

The total amount adsorbed, n_T , at a given temperature and spreading pressure is only a function of the adsorbed phase compositions x_i and the pure component amounts adsorbed, n_i , at fixed spreading pressure, following

$$n_T = \left[\sum_{i=1}^N \frac{x_i}{n_i^o} \right]^{-1} \quad (14)$$

Where $n_i^o = n_i^{pure}(a_i^o)$ i.e. n_i^{pure} evaluated at $a_i = a_i^o$. The amount adsorbed for each species now can be determined by

$$n_i^{mix} = x_i n_T \quad (15)$$

For the IAST application, the Dubinin-Radushkevich equation is modified to

$$n_i^{pure} = n_{o,i} \frac{\Phi_i}{\Phi_i^o} \exp[\delta_i(T_o - T)] \exp \left[- \left(\frac{RT \ln(a_{s,i}/a_i)}{\tau(\Theta(H', z_{min}) - \Theta^\infty(z_{min}^*))} \right) \right] \quad (16)$$

As the fitted capacity $n_{o,i}$ in the Dubinin-Radushkevich equation includes the network accessibility factor. Here $\Theta(H', z_{min})$ and $\Theta^\infty(z_{min}^*)$ are minimum pore potential at distance z_{min} and z_{min}^* , respectively. While τ is a fluid solid interaction constant. To separate the latter we multiply by the factor of $\frac{\Phi_i}{\Phi_i^o}$

Thus n_i^{pure} represent the isotherm for pure component i , if all available pores (i.e. pores larger than z_{min}) are accessible. Here Φ_i^o is the fraction of the pores that are actually accessible to the probe molecules i . Substitution of equation. (16) into equation (10) leads to the analytical result

$$\Pi_i = \frac{B}{RT} n_{o,i} \frac{\Phi_i}{\Phi_i^o} \exp[\delta_i(T_o - T)] \frac{\sqrt{\pi}}{2} \left[1 - \operatorname{erf} \left[\frac{RT}{B} \ln \left(\frac{a_{s,i}}{a_i^o} \right) \right] \right] \quad (17)$$

which was used in conjunction with Equations. (12)-(15).

In order to test the validity of the proposed model, we used our binary adsorption experiments of ethyl propionate and ethyl butyrate on activated carbons Filtrasorb-400 and Norit ROW 0.8. In our model in order to calculate $\frac{\Phi_i}{\Phi_i^o}$ we used the DFT

based distribution and bimodal gamma function PSD as the normalized pore volume distribution function $f(H)$.

4. Results & Discussion

Binary adsorption equilibrium data have been obtained for the adsorption of ethyl propionate and ethyl butyrate on activated carbons Filtrasorb-400 and Norit ROW 0.8. The effect of the pore network connectivity was taken into account in the prediction of the binary adsorption isotherms using the IAST method. The agreement between the binary component adsorption experimental data and that predicted by our proposed model (equation (17), which is used in conjunction with equations (12) to (15)) is shown in Figures 2.

In general, the model can represent the experimental data fairly well with both PSD as seen in Figure 2. The small difference between the binary isotherms predicted by the model with bimodal gamma function PSD and those using the DFT based distribution is most likely due to the constraint of gamma function bimodal form. In this figure, the symbols represent the experimental data while the solid lines represents the model predicted with equation (17).

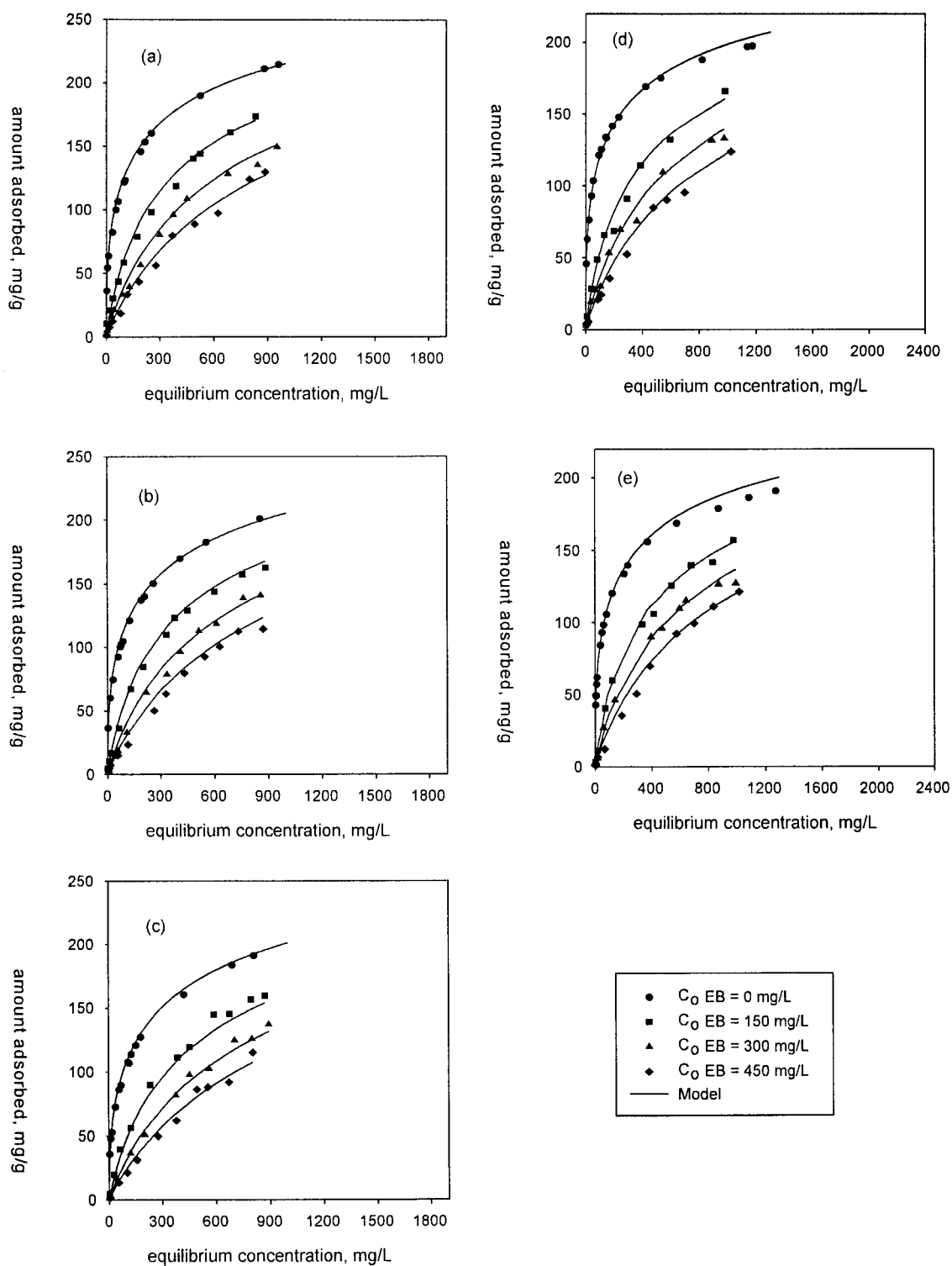


Figure 2. Adsorption Isotherm of Ethyl Propionate in The Presence of Ethyl Butyrate, and Model Results with DFT Based Distribution. Insets are The Model Results with Gamma Function Distribution. (a)-(c) Filtrasorb-400, and (d)-(e) Norit ROW 0.8.

5. Conclusion

The connectivity of the pore network is an important aspect of the structure of porous materials, since it influences their reaction and transport properties. The effect of the pore network connectivity on the prediction of binary component adsorption equilibria has been studied. The Ideal Adsorbed Solution Theory (IAST) is used in conjunction with the modified DR single component isotherm, and is found that the incorporation of the connectivity can improve the performance of multicomponent isotherm model in predicting the experimental binary adsorption equilibria.

Notation

a_i	=	activity of component i
B	=	Parameter
d_{ci}	=	Critical size of component i , nm
$f(H)$	=	Normalized pore volume distribution, $\text{cm}^3/\text{gr.nm}$
H	=	Pore width, nm
H'	=	Center to center distance between carbon atoms on opposing pore walls, nm
n	=	Amount adsorbed, mol/gr
n_T	=	Total amount adsorbed, mg/g
n_{1a}	=	The amount of component 1 adsorbed in region 1, mg/g
n_{1b}	=	The amount of component 1 adsorbed in region 2 to 4, mg/g
n_i^o	=	Amount of pure component i adsorbed at reference activity, mg/g
n_i^{mix}	=	The amount adsorbed for each species, mg/g
$n_{i,\text{tot}}^{\text{mix}}$	=	The total adsorbed amount of component i , mg/g
$n_{o,i}^\infty$	=	Fitted capacity
R	=	Ideal gas constant, J/mol.K
T	=	Temperature, K
T_o	=	Reference temperature, K
Z	=	Coordination number, nm
Z_{\min}	=	Distance between the molecule adsorbate and pore walls, nm
Z_{\min}^∞	=	Distance between the molecule adsorbate and pore walls at infinity
k_i	=	Mol fraction of component i in bulk liquid
δ_i	=	Expansion coefficient of component i (dimensionless)
τ	=	A fluid solid interaction constant
μ_i^a	=	chemical potential of species i in adsorbed phase

μ_i^b	=	chemical potential of species i in bulk phase
μ_i	=	Chemical potential of solute i
Φ_i	=	Fraction of the available pores for component i
Φ_i^a	=	fraction of the pores that are actually accessible to the probe molecules i
Φ^a	=	Fraction of available pores
ϕ	=	Three dimensional spreading pressure
Θ	=	Minimum pore potential
Π_i	=	Spreading pressure

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